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SAMPLING AND ANALYSIS OF SELECTED TOXIC SUBSTANCES TASK II - ETHYLENE DIBROMIDE

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Midwest Research Institute

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SAMPLING AND ANALYSIS OF SELECTED TOXIC SUBSTANCES

TASK II - ETHYLENE DIBROMIDE

September 1975

FINAL REPORT

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16. Abstracts

Ethylene dibromide has recently been reported by the NCI to be a potential carcinogen. Its commercial use is predominately as a scavenging agent for lead in gasoline. A minor usage is a pesticide fumigant. A protcol was developed for the sampling and analysis of ethylene dibromide in ambient air and surface water. The range in concentration of ethylene dibromide in the air and the site where it was collected are as follows: manufacturing sites, 4.2 to 115 $\mu g/M^3$; oil refinery, 0.23-1.65 $\mu g/M^3$; urban locations near retail gasoline stations and with heavy vehicular traffic, 0.069 to 0.11 $\mu g/M^3$. Two water samples collected from streams near an oil refinery and a manufacturing site were found to contain 1.13 and 1.05 ppb ethylene dibromide, respectively. Further work to clarify ambient air levels and to assess whether they may represent a health risk is anticipate, but the very low levels detected to date are not thought to present a significant risk to health.

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BACKGROUND STATEMENT

Ethylene dibromide (EDB), which is also known as 1,2-dibromoethane, is used principally as an additive in leaded gasoline. (It is not needed in unleaded gasoline.) Relatively small quantities of EDB are used as pesticides in soil fumigants (as a nematicide) and in grain and commodity fumigants. Over one hundred EPA-registered pesticides contain EDB. Small quantities are also used as an industrial solvent, and as a chemical intermediate. Five U.S. companies - Dow Chemical, Ethyl, Great Lakes Chemical, Northwest Industries (Michigan Chemical), and PPG Industries (Houston Chemical) - produce over 300 million pounds of EDB annually.

The National Cancer Institute issued a "memorandum of alert" on ethylene dibromide in October, 1974. When administered directly into the stomach of rats or mice at the maximum tolerable dose and at half that level, EDB produced stomach cancer at a high rate and with a very short latent period. Tumors appeared as early as ten weeks after the first administration of EDB. This rapid effect is most unusual and may be unprecedented. Details of these experiments can be found in the Journal of the National Cancer Institute, 51, 1993 (1973). The carcinogenicity of EDB with other routes of exposure has not been determined at the present time, although additional experiments are being designed. However, it may be prudent to consider EDB to be a suspect carcinogen by any route of exposure.

Besides being carcinogenic, EDB is known to cause pneumonia and other lung disorders in rats at 50 ppm, and adversely affect fertility in bulls (4 mg EDB/kg body weight) and in hens (10 ppm EDB in grain). It has also shown mutagenic properties in microorganisms.

Ethylene dibromide is used as a scavenger for lead in leaded gasoline. The chief source of EDB pollution from automotive sources is from evaporative emissions from the fuel tank and carburetor of cars operated on leaded fuel. Emissions from these sources have been estimated to range from 2 to 25 mg/day for 1972 through 1974 model-year cars. Emissions from pre-1972 cars would be somewhat higher than these estimates. EDB is not expected to be emitted in the exhaust because it is not expected to survive the combustion process.

Ethylene dichloride is also used as a scavenger along with EDB. Although ethylene dichloride is cheaper than EDB, it alone cannot be used satisfactorily because the lead chloride formed is not sufficiently volatile to keep all parts of the combustion chamber free of lead deposits. Although ethylene dichloride is probably less of a hazard than EDB, the health implications of exposure to it are not fully understood.

The increased use of unleaded gasoline in some 1975 and later model-year cars, in conjunction with possible regulations to lower the average lead content of gasolines, should reduce any possible risks associated with the use of EDB as an additive to gasoline.

The very limited and preliminary air monitoring data set forth in this report show air concentration values of 0.07-0.11 $\mu g/m^3$ (about 0.01 ppb) in the vicinity of gasoline stations along traffic arteries in three cities (Phoenix, Los Angeles, and Seattle), 0.2-1.7 $\mu g/m^3$ (about 0.1 ppb) on the property of an oil refinery in Kansas City, and 90-115 $\mu g/m^3$ (10-15 ppb) at EDB manufacturing sites in Arkansas. This suggests that EDB is present in ambient air at very low concentrations. Suitable sampling sites associated with pesticidal uses of EDB were not identified in this study. Further work to clarify ambient air levels and to assess whether

they may represent a health risk is anticipated, but the very low levels detected to date are not thought to present a significant risk to health.

Concentrations on the order of 1 ppb of EDB were found in two samples from streams of water on industrial sites. Although EDB is not thought to be a serious water pollutant, this matter will be further investigated. Ethylene dibromide is not believed to accumulate in the environment. Limited information suggests that it degrades at moderate rates in both water and soil.

Office of Toxic Substances
Environmental Protection Agency
September 29, 1975

EPA 560/6-75-001

SAMPLING AND ANALYSIS OF SELECTED TOXIC SUBSTANCES
TASK II - ETHYLENE DIBROMIDE

by

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EPA Contract No. 68-01-2646

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For

Environmental Protection Agency

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I. SUMMARY AND CONCLUSIONS

A limited sampling and analysis program was conducted to determine if ethylene dibromide (EDB) is present in ambient air or surface water. The protocol for sampling air utilized a sampling medium of Tenax-GC® resin at dry ice temperature to trap EDB. The sampling train was assembled with a filter and a drying tube ahead of the collecting medium. A critical orifice was placed after the sampling train to insure an air flow of 1 liter/min. A single Tenax-GC® trap was demonstrated to be 94% effective in trapping EDB. EDB was extracted from the Tenax-GC® with hexane for analysis. Water samples were extracted twice with hexane using V_{aq}/V_{hexane} ratio of 20:1. The hexane extracts were analyzed for EDB by electron capture gas chromatography. Several column packings were utilized.

The three general categories of sampling locations selected for this study were: manufacturing sites, oil refineries, and heavily trafficked urban areas. Sampling and analysis revealed 4 to 115 $\mu g/M^3$ of EDB in ambient air near the manufacturing sites, and 0.23 to 1.65 $\mu g/M^3$ at the oil refinery, near a bulk transfer site. Samples collected in Phoenix, Arizona, Los Angeles, California, and Seattle, Washington, were found to contain 0.069 to 0.11 $\mu g/M^3$ of EDB. The relative concentrations in the three general areas were in the order expected. Water samples taken from small streams below the oil refinery and at the downstream edge of a manufacturing site contained 1.13 and 1.05 ppb of EDB, respectively. The stream at the oil refinery is directed into the company's biodegradation ponds. The stream coming off the manufacturing site is quite small and nearly stagnant.

II. INTRODUCTION

Ethylene dibromide (1,2-dibromoethane) is commercially produced by reaction of ethylene and bromine. Most of the United States production sites are located near the brine fields around Magnolia and El Dorado, Arkansas. The brine, rich in bromide salts, provides a ready supply of bromine. The known major producers[1] are listed in Table 1.

Table 1. ETHYLENE DIBROMIDE PRODUCERS IN THE UNITED STATES

Company	Location
Dow Chemical, USA	Magnolia, Arkansas Midland, Michigan
Ethyl Corporation	Magnolia, Arkansas
Great Lakes Chemical Corporation	El Dorado, Arkansas
Northwest Industry, Inc.	El Dorado, Arkansas
PPG Industry, Inc.	Beaumont, Texas

Historically, ethylene dibromide has been used commerically as a gasoline additive and as a fumigant. Its value as a gasoline additive is to serve as a scavenger agent for lead released in the combustion process. The concentration of EDB in gasoline is variable but is on the order of 0.025% (wt/vol).[2]

The second use of EDB has been as a fumigant. It has been used in disinfecting fruits, vegetables, foodgrains, seeds, seedbeds, mills, and warehouses.[3] It has also been shank injected[4] into soil to combat nematodes in tobacco fields. While normally used by commercial fumigators on large installations in the United States, it is possible that EDB is used at the individual farm level[3] for fumigating grains in small containers.

The level of application is very dependent upon the nature of the specific fumigation task. Frequently, EDB is added in a mixture with other fumigants such as ethylene dichloride, carbon tetrachloride, carbon disulfide or methyl bromide.[5,6] The nature of the mixture effects the application rate. Typical of the recommended doses are: 1 to 5 gal. of 7% EDB

per 1,000 bushels stored grain;[7] 1.5 to 3.0 lb of EDB per 1,000 ft^3 of space; 4.5 to 6 gal. of 83% EDB per acre of tobacco fields.[4] Commercially fumigated grain showed residues of EDB from less than 0.01 to 6.1 ppm.[8] The EDB residue level on grains fumigated in laboratory experiments did not change significantly in 7 weeks after application.[7]

Very little is known about the presence of EDB in ambient air or surface water. It appears that EDB has not been previously reported to be present in urban atmospheres[9] or public drinking waters.[10] A potential exists, however, for the introduction of EDB into the atmosphere. The most probable sources are: evaporative loss from leaded gasoline both from retail stations and automobiles; incomplete combustion; evaporative loss from leaded gas mixing, storage and bulk transfer locations; granaries or fields fumigated with EDB containing fumigants; fumigant mixing, storage and bulk transfer locations; as well as manufacturing, storage and bulk transfer locations of EDB. Thus, a potential exposure may exist not only for a few hundred people at isolated manufacturing sites but also for the entire urban population.

This monitoring program was designed to answer the following questions:

1. Is EDB present as an environmental pollutant in either ambient air or surface water?

2. How great is the exposure potential at critical manufacturing and high use locations?

III. SCREENING AND SELECTION OF SAMPLING SITES

The task called for the selection of sites where critical exposure to EDB would be anticipated. The following were specified as sampling sites:

1.	Manufacturers	- 2 Sites
2.	Granaries	- 2 Sites
3.	Soil fumigation	- 1 Site
4.	Urban areas	- 3 Sites
5.	Leaded gasoline storage and bulk transfer	- 1 Site

Ambient air and surface runoff water, if available, were to be collected at all locations.

The normal factors to be considered in site selection would include, among others, production volume, degree and method of discharge, control, the nature of the treatment facilities, the competence and cooperativeness of the facility management, meteorological factors, population densities and nature of nearby industrial operations. For high priority situations, such as in this case, all adverse factors effecting a quick response time were heavily weighted. Such factors included: site and equipment modifications required prior to sampling; administrative problems encountered in gaining access to specific sites; and the effect of other externalities, e.g., climatic conditions, on the feasibility of immediate sampling. All sites were selected to represent the maximum release of toxic materials rather than a representative nationwide exposure of man and/or the environment.

A. Manufacturing Sites

All known United States producers of EDB are listed in Table 1.[1/] Two industrial facilities owned by Dow Chemical, USA and Ethyl Corporation, were selected as sampling locations. The two sites are in close proximity to each other at Magnolia, Arkansas.

B. Granaries

Since EDB has been used for postharvest fumigation of sorghum, wheat and corn, an intensive attempt was made to locate a granary using

this method of pest control. The facilities contacted and responses elicited are listed below.

1. Ed Sorenson, Manager, Farmaro Elevator, Hutchinson, Kansas - "No EDB used in Hutchison."

2. Don Anderson, Manager, Farmers Coop, Wellington, Kansas - "No EDB used, phostoxin is the present substitute."

3. Manager, Wolcott-Lincoln Elevator, Kansas City, Missouri - "Will not use EDB."

4. Manager, Van Watters and Rogers Elevator, Salt Lake City, Utah - "A gas, probably methyl bromide will be used."

5. Dr. Dewitt, Extension Agent, Iowa State University, Ames, Iowa - "EDB not used on corn in Iowa."

6. Mildred Mayer, Farmers Coop, Clovis, New Mexico - "EDB is not used; phostoxin is used."

7. Bob Strader, New Mexico Mill and Elevator, Clovis, New Mexico - "I have used Dowfume EB-5 in the past but do not expect to do so this year."

8. Mr. Sullens, Industrial Fumigants, Kansas City, Missouri - "EDB is used generally in spot fumigation of milling equipment but phostoxin is used for granaries."

9. Research Products, Inc. (Commerical Fumigator), Kansas City, Missouri - "We do not use EDB."

C. Soil Fumigation

It had been reported that EDB containing fumigants are used for postharvest fumigation of potato fields in Wisconsin and Idaho, and tobacco fields in Connecticut. Our investigation, summarized below, did not identify any significant users of EDB-containing fumigants in these areas.

Our contacts and their responses are listed below.

1. L. K. Binning, University of Wisconsin, Horticulture Department, To his knowledge, EDB fumigants are not used by the tarping technique on the Wisconsin potato fields. He believed that a small quantity was used on seed beds.

2. W. Sparks, University of Idaho, School of Agriculture, To his knowledge, very little EDB containing fumigant is used in Idaho, due mainly to the expense. However, when EDB is used, it is injected 1 to 2 in. below the soil surface.

3. Gordon Taylor, State Department of Agriculture, Windsor Experimental Station, Connecticut, He indicated that Dowfume W-85 has been shank injected into shade tobacco fields at the rate of 4 to 6 gal/acre.

4. Robert Borg, Professional Fumigator, West Suffield, Connecticut, He believes Dowfume W-85 to be inadequate and he no longer uses it.

D. Urban Areas

Ethylene dibromide is an additive to leaded gasoline at a rate approximating 0.025% (wt/vol). Consequently, EDB may be introduced into the urban atmosphere by evaporative losses from automobiles and retail gasoline stations and possibly from incomplete combustion. To explore this possibility, sampling sites were chosen because they are heavily trafficked, are adjacent to several retail gasoline stations, and are in downtown areas or other areas having heavy pedestrian use. The sites were also chosen to represent a wide range of light and temperature conditions. The sites selected for sampling were Phoenix, Arizona, Los Angeles, California, and Seattle, Washington.

E. Leaded Gasoline Storage and Bulk Transfer

Generally, lead and related additives are mixed with gasoline at a refinery site. The gasoline is stored in large tanks and ultimately transferred into trucks for delivery to retail stations. Loading may be through the top or through the bottom of the trucks. Loss by volatilization is greater when trucks are top-loaded. The oil refinery at Sugar Creek, Missouri, was chosen as a representative storage and transfer facility and two locations in close proximity to the mixing shed, gasoline storage tanks and the bulk transfer dock were established as the sampling points.

IV. DISCUSSION OF SAMPLING SITES

A. Manufacturers

The Dow production facilities were located approximately 10 miles west of Magnolia, Arkansas. The air sampling site location, with respect to the EDB production facilities, is shown in Figure 1. The site was approximately 250 ft northwest of the production area and situated on the inner edge of the access road. The sampling probe was 6 ft high and directed into the wind as well as toward the facility. Throughout the sampling period the wind direction was constant (from the southeast) but velocity varied from 0 to 5 mph for the period of 0900 to 1600. Rain occurred from 1600 to 1700, however, sampling had been terminated at 1430. There was no detectable wind from 1700 to 1930. Temperatures at selected sampling times were 74°F (0900), 90°F (1115), 100°F (1320), 89°F (1600) and 84°F (1900).

Water samples were collected at two sites on the Dow property (Figure 2). The streams, normally slow moving, were flowing rapidly due to a 1.7 in. rainfall the previous night.

A site map of the Ethyl Corporation facility, located approximately 10 miles south of Magnolia, Arkansas, is shown in Figure 3. The sampling equipment was placed approximately 100 ft north northeast of the EDB facilities, adjacent to the plant administration building. The sampling probe was again 6 ft high and directed into the wind. No rain was recorded at this site, although the wind behavior was identical to that at the Dow site. Temperatures at selected times were 94°F (1045), 80°F (1300), 87°F (1530) and 85°F (1735). The relative humidity at both the Dow and Ethyl sites ranged from 65 to 100%. This variable was not determined at any of the other sites. No water samples were available.

B. Granaries

No samples were obtained due to the reasons previously discussed.

C. Soil Fumigation

No samples were obtained due to the reasons previously discussed.

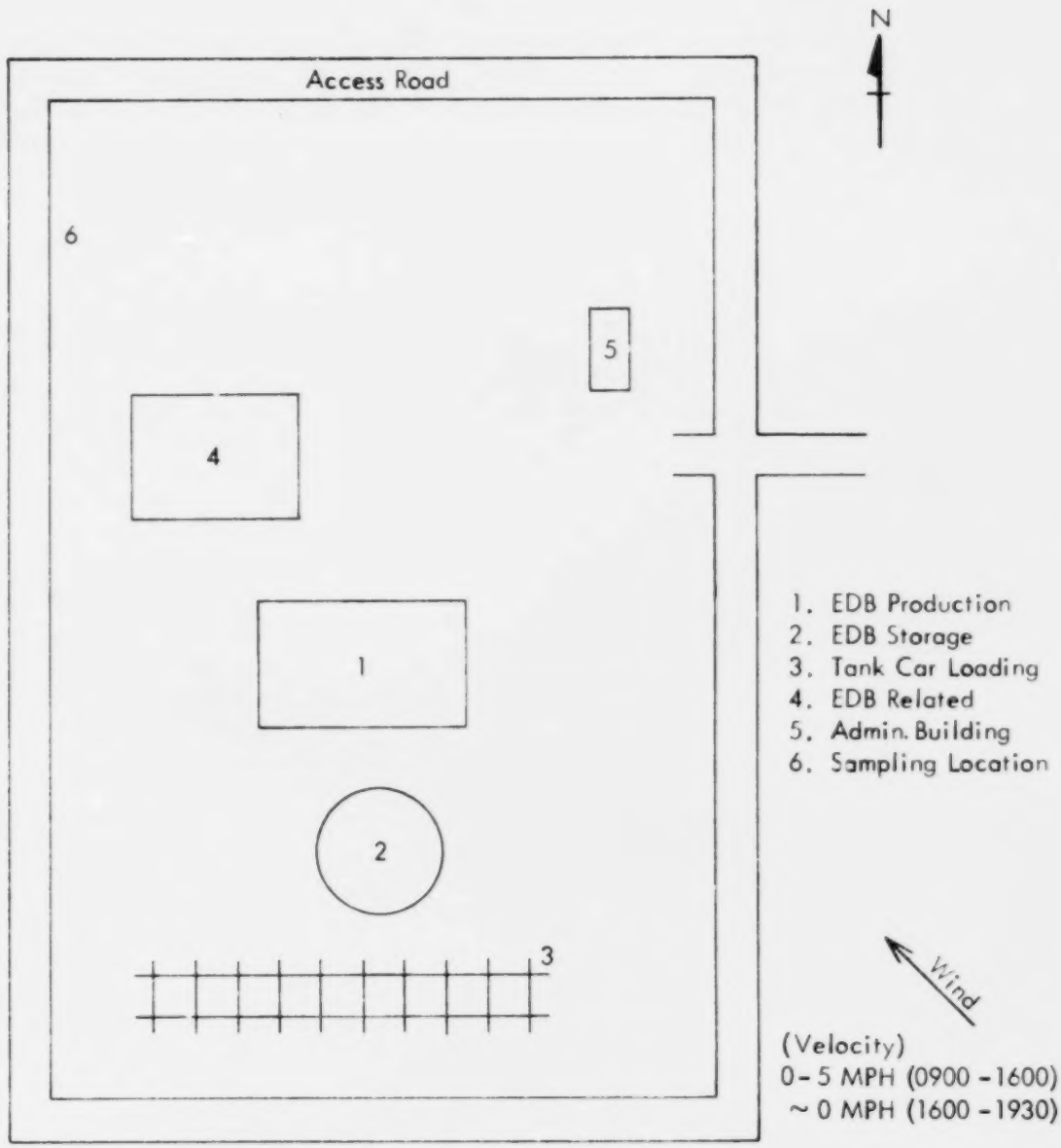

Figure 1. Air sampling [illegible]ation - Dow Chemical, Magnolia, Arkansas

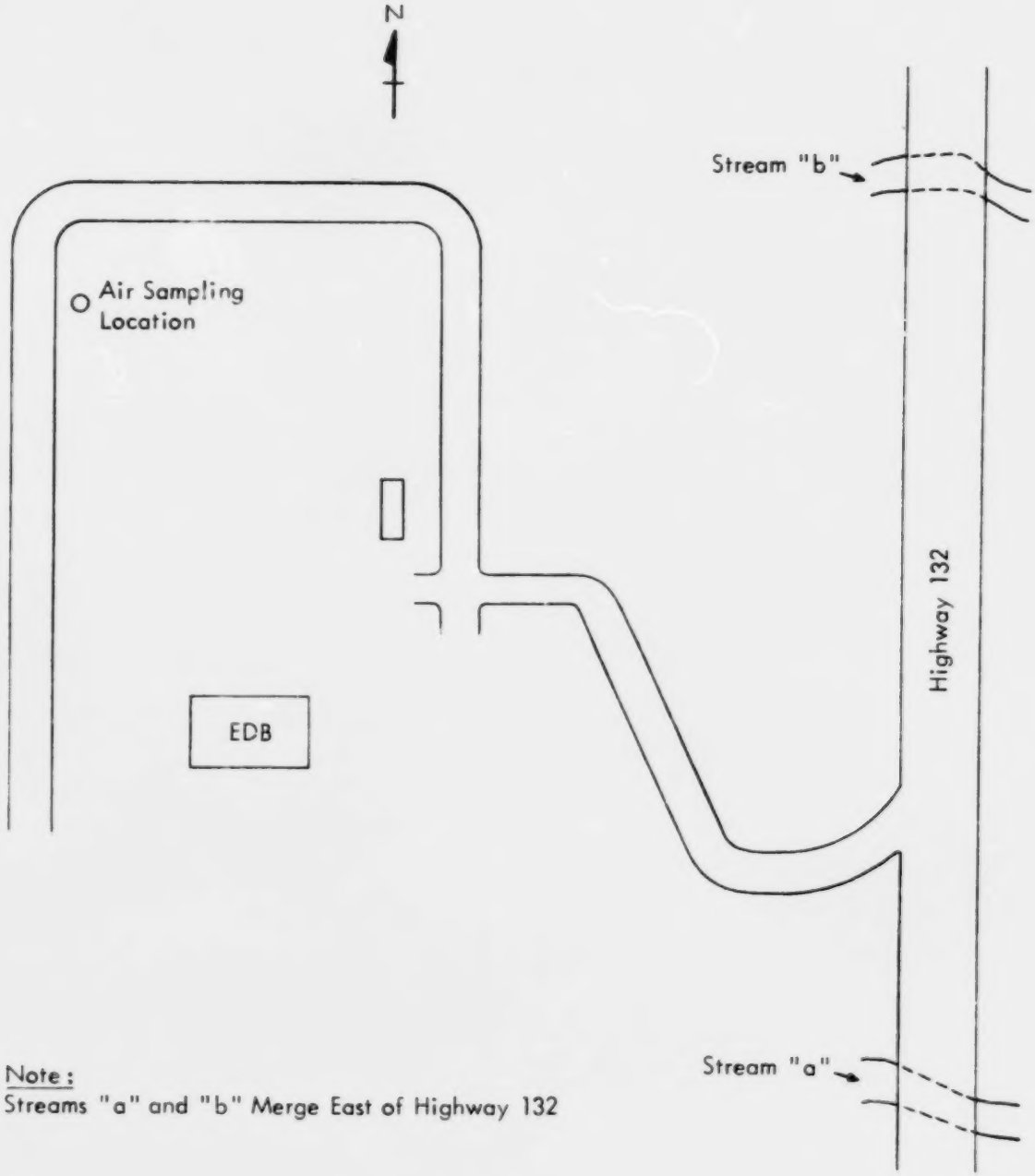

Figure 2. Water sampling locations - Dow Chemical, Magnolia, Arkansas

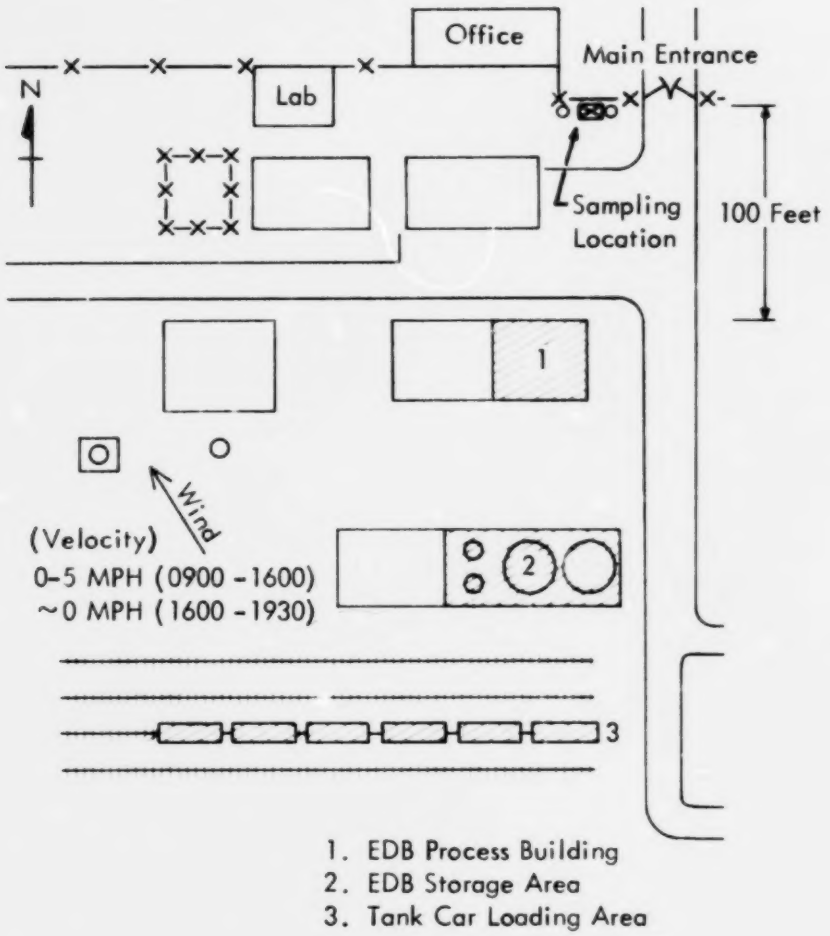

Figure 3. Air sampling location - Ethyl Corporation, Magnolia, Arkansas

D. Urban Areas

1. Phoenix, Arizona: A map of Phoenix showing the general location of the air sampling site is presented in Figure 4. A more detailed description of the specific site is given in Figure 5. The sampler located on the sidewalk at 1804 Camelback Street was set at a height of 6 ft and directed into the wind. Camelback is a six-lane street carrying an average traffic load of 36,000 vehicles per day. Six retail gasoline stations located within three city blocks of the site sell about 475,000 gal/month. The vicinity may be characterized as a retail shopping area located in a residential district. A light wind blew from the east during the period of 0700 to 1200 and shifted 180 degrees continuing from the west during the period of 1200 to 2400. Temperatures during the sampling period were 99°F (0700), 100°F (1200), 119°F (1520), 118°F (1800) and 100°F (2400).

2. Los Angeles, California: The general location of the air sampling site is shown in Figure 6. A detailed drawing of the actual sampling location is presented in Figure 7. Sampling equipment was located at the pay booth of the Kirkaby Center parking lot on Lindbrook Avenue in Westwood Village. The site was approximately 100 ft east of Westwood Street and was 1 block north of Wilshire Boulevard. The daily vehicular traffic loads were 26,000 and 53,000 for Westwood and Wilshire Boulevard. Four major retail gasoline stations were located within approximately 500 ft of the sampler. As before, the probe was at a height of 6 ft and directed into the wind. A light westerly wind was observed from 0800 to 1400. At this time it shifted and continued in an easterly flow from 1400 to 2000 hr. Temperatures during the sampling periods were 79°F (0800), 90°F (1200), 91°F (1600) and 78°F (2000).

3. Seattle, Washington: A map showing the general location of the air sampling site is found in Figure 8. A detailed drawing of the two sampling locations established in Seattle is shown in Figure 9. One location was approximately 200 ft south of 45th N.E. on Roosevelt Way, and situated by the sidewalk on the University Datsun car lot. The second location was approximately 100 ft north of 45th N.E. on Roosevelt Way and placed by the sidewalk on the University Chevrolet car lot. In both cases, the probe was set at a height of 6 ft and directed into the wind. The vehicular traffic loads were reported as 32,000 and 9,000/day for 45th N.E. and Roosevelt Way, respectively. Three major retail gasoline stations are located on 45th N.E., all within approximately 300 ft of the sampling sites. The wind was light and from the southwest during the sampling. Temperatures during the sampling periods were 58°F (0730), 61°F (1110), 67°F (1500) and 65°F (1900).

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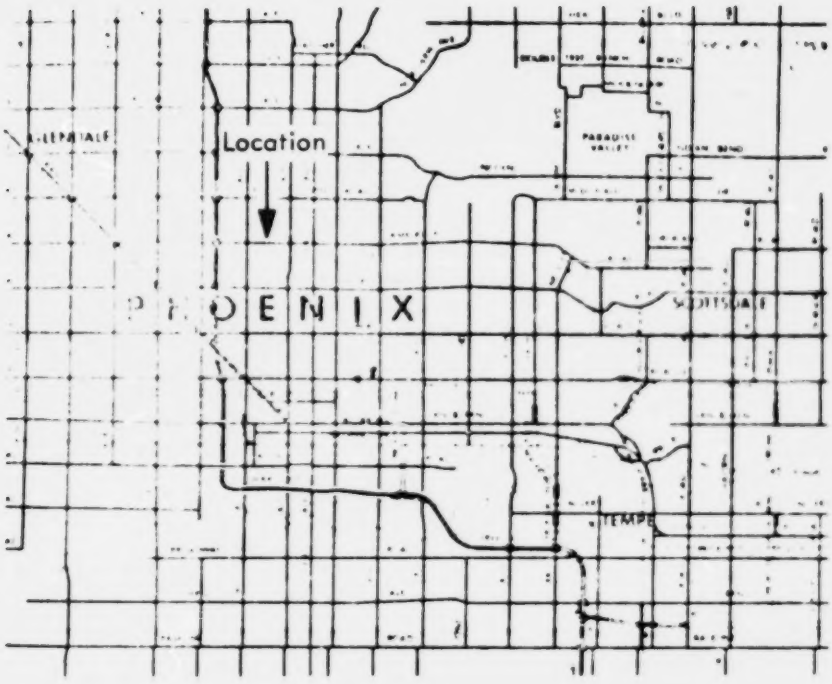

Figure 4. Air sampling site - Phoenix, Arizona

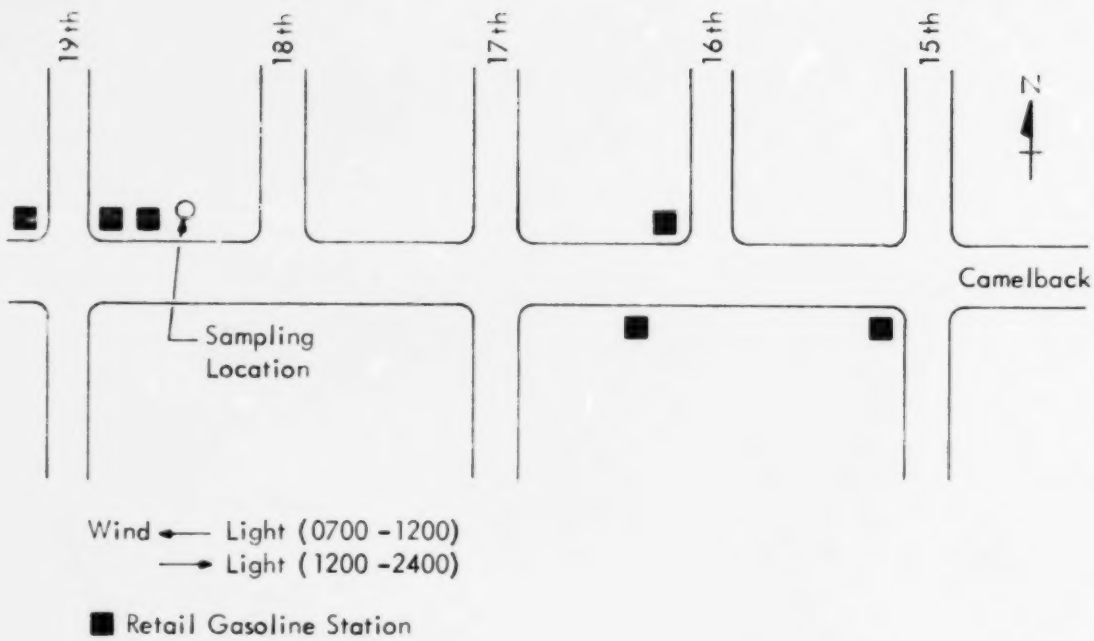

Figure 5. Air sampling location - Phoenix, Arizona

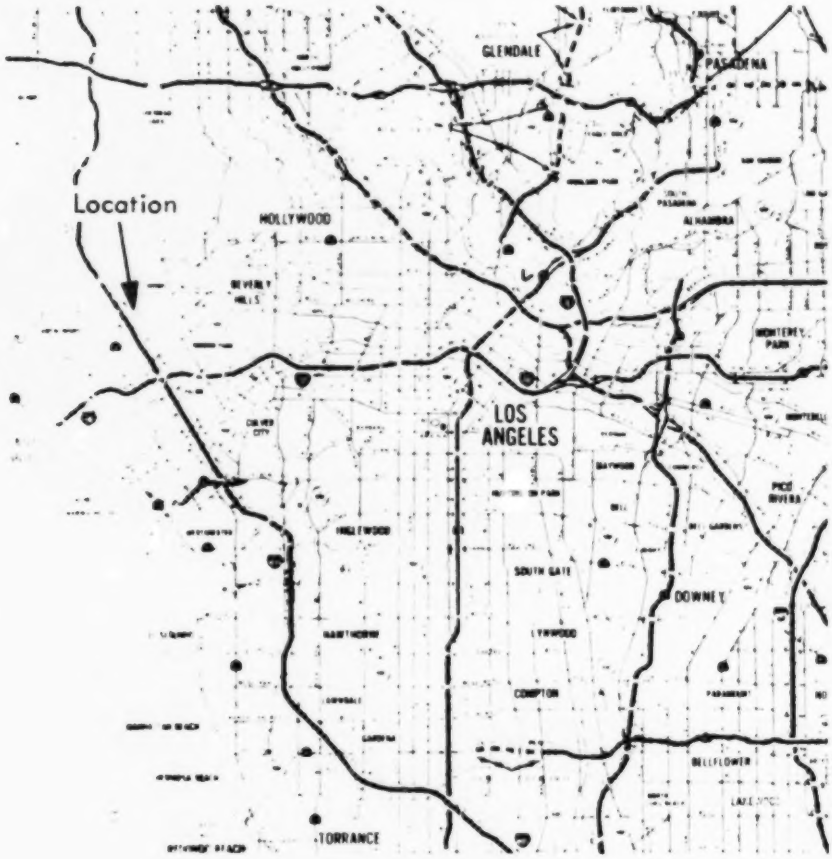

Figure 6. Air sampling site - Los Angeles, California

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Figure 7. Air sampling location - Los Angeles, California

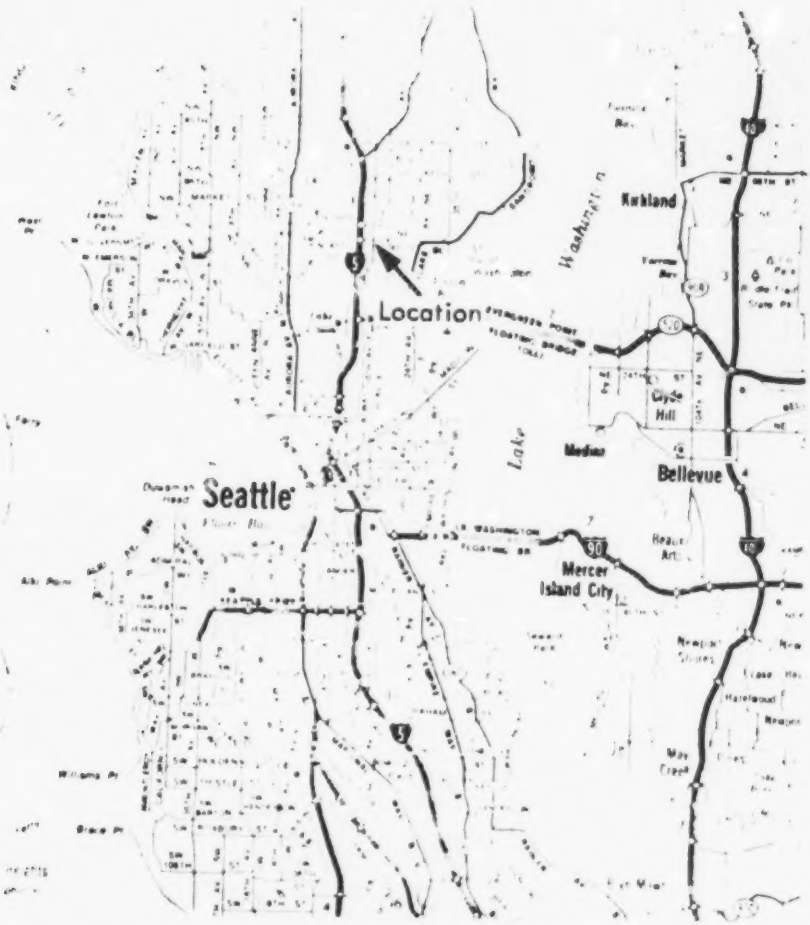

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Figure 8. Air sampling site - Seattle, Washington

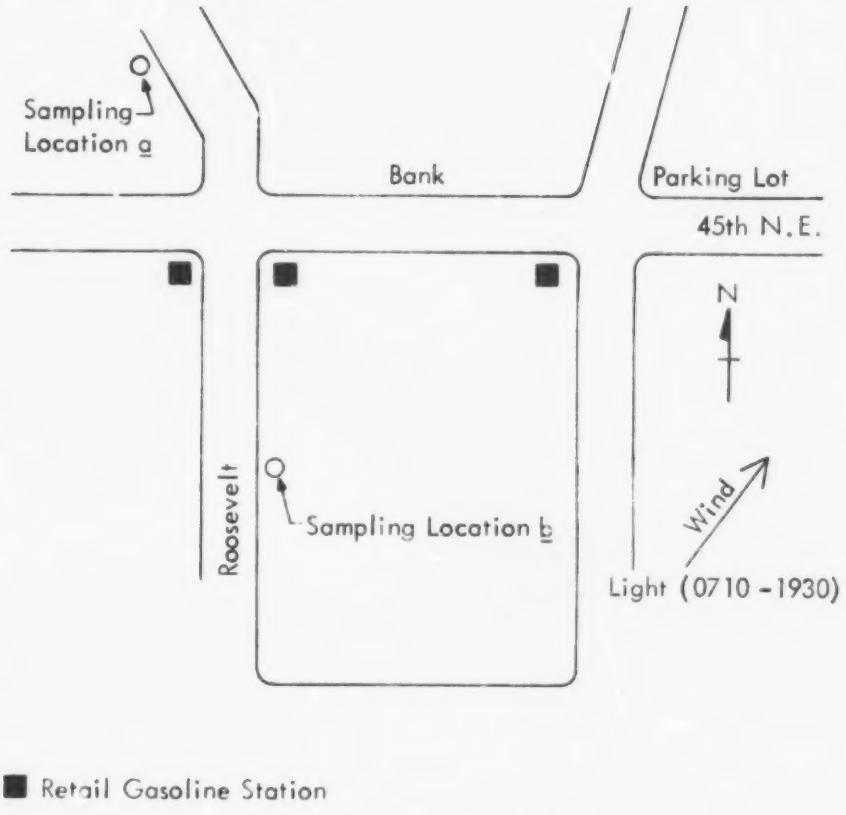

Figure 9. Air sampling locations - Seattle, Washington

E. Leaded Gasoline Storage and Bulk Transfer

A map depicting the location of the two air sampling locations and the stream used for water sampling appears in Figure 10. Air sampling location "a" was approximately 50 ft south of the tank truck loading facilities at which loading is done through the top with an open stream. Location "b" was at the "process laboratory," 400 ft north of the bulk transfer facilities and was used only during July 31 to August 1 sampling. During the entire sampling period the wind was from the south at 5 to 10 mph. Temperatures during the sampling period were, on July 31, 77°F (0800), 90°F (1200), 94°F (1600) and 88°F (2000), and on August 1, 72°F (0800).

During repeat sampling on August 15, the wind was from the north at 5 to 10 mph. Temperatures during the sampling period were 80°F (0800), 82°F (1200) and 85°F (1600). The gasoline transfer facility was open and used 24 hr/day.

The water sample was taken from a small stream, designated as "c," that surfaced south of the bulk loading station, and was then covered and channelled into the company's biodegradation ponds.

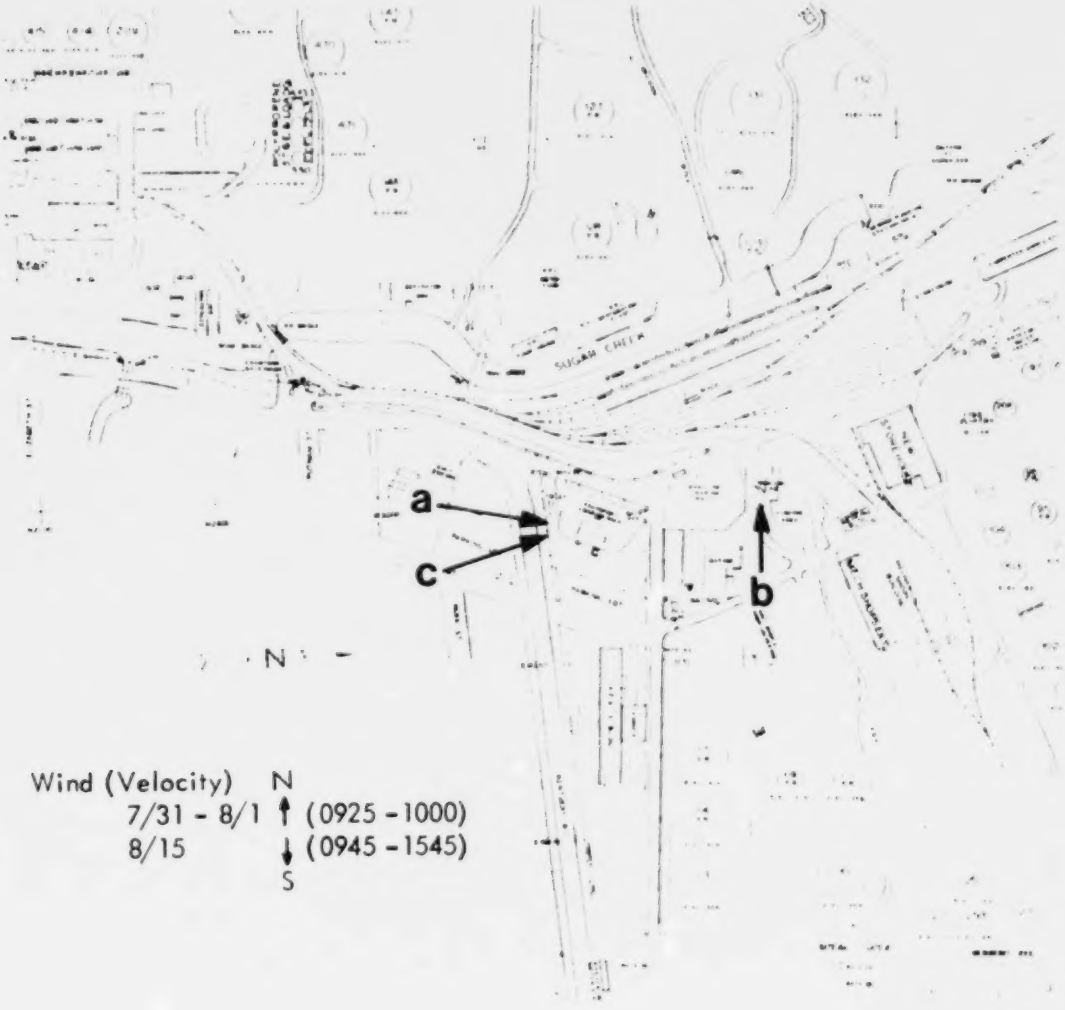

Figure 10. Air and water sampling locations - oil refinery, Sugar Creek, Missouri

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V. DEVELOPMENT OF SAMPLING AND ANALYSIS PROTOCOL

A. Method Development and Evaluation

1. Air: Most of the published literature on the sampling and analysis of EDB has been related to its use as a fumigant. Interstitial air concentrations in closed bins or silos have been determined by analyzing gas samples with flame ionization gas chromatography.[7] The limit of detection by this technique has been reported as 2 µg/liter (0.24 ppm). Based on a reported sensitivity of 50 pg[7] for electron capture detection gas chromatography, the calculated limit of detection by direct gas sampling would be 50 ng/liter (0.006 ppm). In this study it was anticipated that in most instances the EDB concentrations in ambient air samples would be considerable lower than either of the above detection limits.

Therefore, an analytical procedure was required that concentrated the EDB present in a relatively large volume of air. Sampling periods of up to 24 hr were anticipated since neither the actual source of emissions nor the emission patterns were known or predictable.

The initial approach to sampling air for EDB was to use a Tenax-GC® trap at ambient temperature. Experiments run under laboratory conditions indicated that good recovery of EDB should be possible. A stream of helium at 200 ml/min for 5 hr was used to evaporate and carry 500 ng of EDB into a Tenax-GC® trap at ambient temperature. Recovery was 84%. Therefore, Tenax-GC® at ambient temperature was used to sample the oil refinery. Two Tenax-GC® traps were connected in series and air was drawn through at 1 liter/min. EDB was found on both Tenax-GC® traps. Under field conditions EDB either was not stopped or was migrating through the tubes. Additional laboratory experiments indicated that EDB migrated through the columns. A glass tube containing 2,000 ng EDB in hexane was connected to two Tenax-GC® traps (T-1 and T-2) in series. Helium was passed through at 1 liter/min. After 2 hr, the second trap, T-2, was replaced by T-3. Two hours later, T-3 was replaced by T-4. T-4 was left in place for 4 hr. All the tubes were extracted and analyzed for EDB.

Tube	EDB
T-1	160 ng
T-2	568 ng
T-3	645 ng
T-4	370 ng

While about 60 to 70% of the EDB was originally stopped by T-1, under the constant flow of helium, EDB migrates down and out of the tube. Thus, it was concluded that at ambient temperatures Tenax-GC® was ineffective for long term air sampling of EDB.

To be certain that EDB would be retained by the Tenax-GC® traps, the tubes were cooled with dry ice. This modified cryogenic technique has been used to trap vinyl chloride on Tenax-GC®.[10] Silica gel drying tubes were inserted ahead of the Tenax-GC® trap to remove water vapor and avoid the formation of ice plugs. The efficiency of the air sampling train shown in the air sampling protocol was evaluated by the following experiment. A glass tube containing 500 ng EDB was connected to the drying tube and two Tenax-GC® tubes were cooled by dry ice. Helium was passed through at a rate of 750 ml/min for 4 hr. The tubes and their contents were then extracted with hexane and analyzed for EDB by the procedure described in the analytical protocol. The results of duplicate runs are as follows:

	Run 1	Run 2	Average
Percent EDB recovered by first extraction	73	79	76
Percent EDB recovered by second extraction	21	14	18
Percent EDB retained by drying tube	0	0	0
Percent EDB retained by first Tenax-GC® tube	94	93	94
Percent EDB retained by second Tenax-GC® tube	0	0	0

The first Tenax-GC® trap was extracted twice in this experiment. In analyses of field samples, only one extraction was used and therefore a recovery factor of 1/0.76 or 1.3 has been applied to the results. As seen in the above results, EDB was not retained by the drying tube and did not pass through the first Tenax-GC® tube. The procedure works well in moderate humidity ranges. With high humidity, the drying tubes can be readily saturated and will require periodic changing.

The hexane extracts from the first sampling of the oil refinery (July 31 to August 1) were reanalyzed 6 days after the initial analysis. A considerable decrease in the amount of EDB present was observed (see Table 2). These samples had been stored in a refrigerator. Since degradation was rapid, all subsequent samples were stored in a freezer at -13°C. This procedure appeared to stabilize the samples. The analysis of hexane extracts containing EDB was done by gas chromatography using an electron capture detector. The electron capture detector is extremely sensitive to EDB and can detect as little as 1 to 2 pg/injection. Calibration plots were found to be linear from 20 to 1,000 pg/injection. All samples were first chromatographed on Carbowax 20M according to the conditions listed as Column 1 in Table 3. Additional columns were used for confirmation of identity. Chromatographic conditions are also listed in Table 3.

Table 2. RESULTS OF EDB ANALYSIS
(Air Analysis)

Site location	Date	Sampling time, temperature min-max	Volume sampled (ℓ)	Filter (ng)	Drying tube (ng)	Tenax, ng ambient 1st	Tenax, ng ambient 2nd	Tenax, ng dry ice 1st	Tenax, ng dry ice 2nd	EDB µg/m³	EDB ppb	EDB[c] µg/m³	EDB[c] ppb
Oil Refinery	7/31-												
a. Bulk loading	8/1	a. 0925-1000	1,364	207	-	710	780	-	-	1.09	0.131	1.42	0.170
				ND[a]	-	(180)[a]	(120)[a]			(0.22)[a]	(0.026)[a]	(0.29)[a]	(0.034)[a]
b. Process lab		b. 0945-0945 72-94°F	1,318	220	-	725	816	-	-	1.27	0.152	1.65	0.20
				ND[a]	-	(21)[a]	(10)[a]			(0.024)[a]	(0.0029)[a]	(0.031)[a]	(0.0038)[a]
Oil Refinery	8/15												
a. Bulk loading		a. 0945-1545 80-85°F	174	ND	ND	-	-	31	ND	0.18	0.022	0.23	0.029
Phoenix	8/5	a. 0700-2400 99-119°F	765	ND	ND	-	-	41	ND	0.053	0.0064	0.069	0.0083
Los Angeles	8/7	a. 0800-2000 78-91°F	641	ND	ND	-	-	55	ND	0.086	0.010	0.11	0.013
Seattle	8/20												
a. N of 45th street		a. 0730-1930	715	ND	ND	-	-	45	ND	0.063	0.0076	0.082	0.0099
b. S of 45th street		b. 0710-1945 60-67°F	705	ND	ND	-	-	45	ND	0.064	0.0077	0.083	0.010
Dow	8/26	a. 0900-1330	116	ND	ND	-	-	9,400	ND	81.0	9.72	105.0	12.6
		b. 1330-1430	43.8	ND	-	3,750	115	-	-	88.2	10.6	115.0	13.8
Ethyl Corporation	8/26	a. 1045-1530	113.8	ND	ND	-	-	7,900	ND	69.4	8.32	90.2	10.8
		b. 1530-1730[b]	80.8	ND	ND	-	-	260	ND	3.2	0.38	4.2	0.49
		c. 1730-1845	46.9	ND	ND	-	-	330	ND	7.0	0.84	9.1	1.09
		d. 1630-1730	44.4	ND	-	360	ND	-	-	8.1	0.97	10.5	1.26
		e. 1730-1830 74-100°F	43.5	ND	-	515	ND	-	-	11.8	1.42	15.3	1.85

a/ Second analysis, 6 days later.
b/ Rain in area - 1600-1700
Wind - SE 2-5 mph 0900-1700, than ~ 0
c/ Corrected by multiplying by 1.3 to account for actual recovery of 76%.
ND = Not detected.

Table 3. GAS CHROMATOGRAPHIC COLUMNS AND CONDITIONS COLUMN

	1	2	3	4
Packing	5% Carbowax 20 M on 80/90 Anakron	5% QF-1 on 100/120 Sulpelcoport	5% DEGS on 80/100 Chromosorb W	1% OV-101 on 100/120 Chromosorb G-HP
Column Dimensions	6 ft x 1/8 in. stainless steel	6 ft x 1/4 in. stainless steel	6 ft x 1/8 in. stainless steel	6 ft x 1/8 in. stainless steel
Column Temperature	115°C	75°C	80°C	70°C
Injector Temperature	205°C	205°C	205°C	205°C
Detector Temperature	210°C	210°C	210°C	210°C
Flow Rate, He	32 ml/min	32 ml/min	20 ml/min	20 ml/min
Retention Time	4.1 min	4.0 min	2.4 min	1.38 min

2. Water: No reports of EDB being present in surface waters were found in the literature. Several procedures for multiresidue analyses of EDB on grains were expected to be satisfactory for analyzing water. In one procedure[5] grains coated with EDB were added to water, toluene was added, and the EDB was quantitatively removed by steam distillation. Alternately, EDB can be removed by a nitrogen sparge of a boiling solution.[6] In this procedure water present in the gas stream was removed by a drying trap of Chromosorb W. The EDB was then trapped in isooctane held at -80°C.

A simpler procedure than the above was desired. It was determined that water samples containing EDB could be quantitatively extracted by hexane using two extractions at a V_{aq}/V_{org} ratio of 20:1. Five-hundred milliliters of water containing 5 ppb EDB was subjected to sequential extractions; recoveries of 82 and 20% were obtained, yielding a total recovery of 102%.

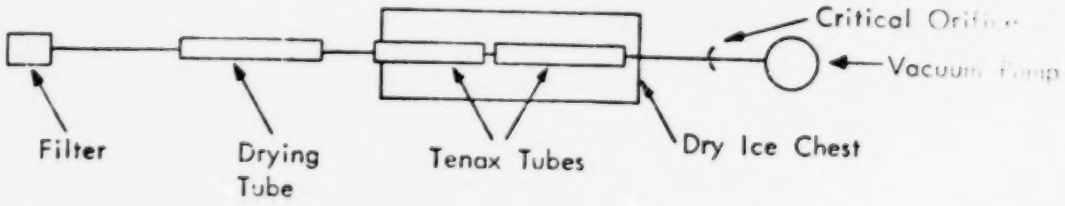
If necessary, the extracts can be reduced in volume using a Kuderna-Danish evaporator. Two 500 ml water samples containing 0.1 ppb EDB were extracted with two 25-ml portions of hexane. The volume of the hexane was reduced to 5.0 ml by the evaporator. Recovery was 47 and 52%.

Attempts to reduce the volume below 5 ml by a slow N_2 stream lead to excessive loss of EDB.

The hexane extracts were analyzed for EDB by the same procedure used for the hexane extracts of the Tenax-GC®.

B. Protocol Adopted

1. Air: The sampling train is shown below:



The filter was a millipore, Type A with a mean pore size of 8 μ. The drying and Tenax-GC® tubes were constructed of glass 15 cm long, 12 cm O.D., 10 cm I.D., and were packed to within 2 to 3 cm of each end. Glass wool previously extracted with hexane was inserted at each end. Minimum lengths of rubber tubing were used to connect the filter and collection tubes. The tubing should be replaced after each use.

Flow rate was controlled by a critical orifice needle at 1 liter/min. Flow rates were checked every 1 to 2 hr. The inlet was positioned at a height of 5 to 6 ft and directed into the wind. All tubes and the filter were stored over dry ice after use. The filter, Tenax-GC® and silica gel were extracted with 20, 20, and 10 ml portions of pesticide grade hexane using an ultrasonic bath. After extraction, the solutions were stored in a freezer until analyzed.

2. Water: Water samples were first filtered if necessary to remove particulate material. The samples were then extracted twice with pesticide grade hexane at a V_{aq}/V_{hexane} ratio of 20. The hexane extracts were combined and diluted to 50.0 ml. The extracts were stored in a freezer until analyzed. If necessary the volume can be reduced to 5.0 ml by use of a Kuderna-Danish evaporator.

VI. RESULTS AND DISCUSSION

Table II summarizes the results obtained for the air samples collected at the sites discussed previously. The oil refinery site was sampled on two separate occasions; the first time using Tenax-GC® at ambient temperature, the second time using the adopted protocol. The hexane extracts held above +4°C showed a time related drop in concentration.

Samples at Dow and Ethyl were collected by both Tenax-GC® traps at ambient and dry ice temperature. The air was sampled for only 1 hr through the ambient temperature Tenax-GC® tubes in order to minimize loss through the tubes. Backup tubes were used to evaluate the efficiency of the first tube. The results obtained at Dow and Ethyl indicated that Tenax-GC® at ambient temperature may be useful for short sampling periods. Breakthrough was only 3% at Dow and EDB was not detected in the second Tenax-GC® tubes at Ethyl.

The results obtained at ambient and dry ice temperatures at both sites agree quite well. For example, comparable samples collected at Dow were found to contain 105 and 115 $\mu g/M^3$. Similar results at Ethyl showed 9.1 and 15.3 $\mu g/M^3$ at dry ice and ambient temperatures, respectively.

The results obtained at Ethyl for the period from 1045 to 1530 hr are similar to those obtained at Dow. At 1600 hr, rain occurred at the Dow site and the wind ceased at both sites. As would be expected, the ambient air levels at Ethyl dropped accordingly. The sampling at Dow had been terminated prior to the rainfall.

The second cold Tenax-GC® trap served as a check of the efficiency of the first trap and as a system blank. EDB was not detected in any of these samples, thus verifying the purity of the hexane and Tenax-GC® resin.

Table IV lists the columns and experimental retention times. The chromatographic peaks observed in the field samples are reported as relative retention values based on the ratio of the retention time of each peak to the retention time of EDB standards. The standards were chromatographed before and after the field samples. The consistency of the ratios provides strong evidence of the presence of EDB in the samples. It was not possible in all cases to obtain second and third column confirmation because of interference of large unidentified peaks from the sample.

Table V summarizes the results obtained from the water samples and lists the retention times where appropriate.

Table 4. RETENTION TIMES

Sites	1 Carbowax 20M t_R	1 Carbowax 20M t_R (STD)	1 Carbowax 20M t_R/t_R (STD)	2 QF-1 t_R	2 QF-1 t_R (STD)	2 QF-1 t_R/t_R (STD)	3 DEGS t_R	3 DEGS t_R (STD)	3 DEGS t_R/t_R (STD)	4 OV-101 t_R	4 OV-101 t_R (STD)	4 OV-101 t_R/t_R (STD)
Oil Refinery												
a. 7/31-8/1	7.58[a]	7.57[a]	1.00	4.18	4.25	0.98	Not used			Not used		
b. 7/31-8/1	7.60[a]	7.57[a]	1.00	-	-	-						
a. 8/15	4.80	4.72	1.02	-	-	-						
Phoenix	4.40	4.33	1.02	4.06	4.00	1.01	Not used			Not used		
Los Angeles	4.33	4.33	1.00	4.10	4.00	1.02	Not used			Not used		
Seattle												
N	5.43	5.47	0.99	-	-	-	Not used			Not Used		
S	5.51	5.47	1.01	-	-	-						
Dow												
a.	4.13	4.13	1.00	Not used			2.44	2.44	1.00	1.38	1.38	1.00
b.	4.13	4.13	1.00				2.44	2.44	1.00	1.38	1.38	1.00
Ethyl												
a.	4.13	4.13	1.00	Not used			2.40	2.44	0.98	1.38	1.38	1.00
b.	4.13	4.13	1.00									
c.	4.13	4.13	1.00									
d.	4.13	4.13	1.00									
e.	4.13	4.13	1.00									

[a] Measured on a 6 ft x 4 mm I.D. glass column packed with 4% Carbowax 20M + 0.8% KOH on Carbopak at 115°C, 30 ml/min. All others at the conditions given in Table 3.

t_R = Retention time in minutes.

Table 5. WATER ANALYSIS[a/] AND RETENTION TIMES

Site Location	Date	Volume Analyzed	EDB (ug)	EDB (ppb)	Carbowax 20 M		
					t_R	t_R(STD)	t_R/t_R(STD)
Oil Refinery[b/]							
c.	7/31	1.0 liter	1.13	1.13	7.58	7.57	1.00
Dow							
a.	8/26	1.0 liter	1.05	1.05	4.13	4.13	1.00
b.	8/26	1.0 liter	0	0	0	0	0

Note: t_R = Retention time in minutes.

a/ Runoff water not available at other sites.

b/ The sample came from a small creek flowing past the bulk loading station. This water is directed into the company's biodegradation ponds.

VII. RECOMMENDATIONS

This study represents only a preliminary investigation of the problem. The imposed time limit did not allow for a comprehensive study. Naturally, many questions are as yet unanswered and should be considered in future programs. For example, temperature, humidity, diurnal, seasonal and geographical effects are not known. The actual source of EDB in the urban areas is not known. The source may be evaporative losses from retail gasoline stations or automobiles, incomplete combustion or combinations of all three factors. The points of emission at the manufacturing sites are, likewise, not known.

EDB levels in the air or water in communities near manufacturing sites should be determined. Apparently, 12% of the EDB produced in the United States is used as a fumigant. This study has not uncovered significant uses of EDB fumigants in the United States or significant export data. It should also be determined where and how the fumigants are mixed, stored and transferred for shipment.

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